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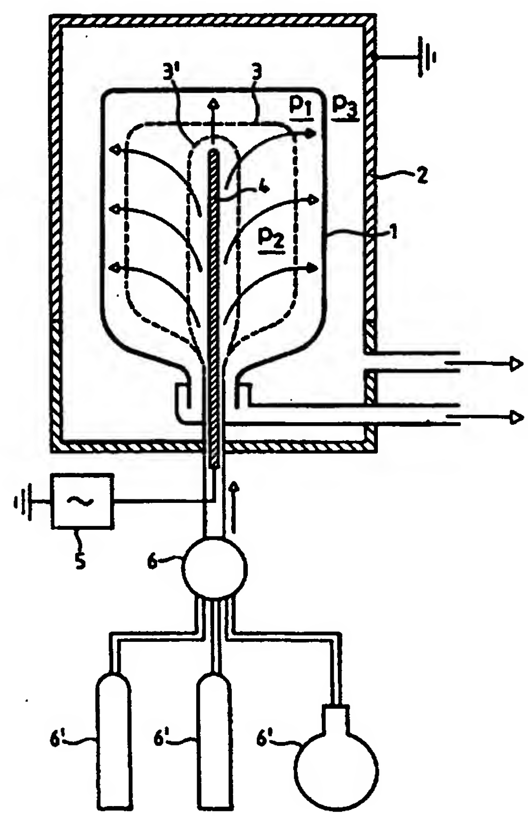
(54) Title: METHOD AND APPARATUS FOR TREATING INSIDE SURFACES OF CONTAINERS

(57) Abstract

The inner surface of a container (1) is treated in a plasma enhanced process, e.g. is cleaned, activated, sterilized or coated, whereby the plasma is confined to a narrow space between an inner member (3) and the inside surface of the container (1). The inner member (3) is adapted in shape to the inside shape of the container, it is hollow and has a porous or perforated wall of a non conductive material or transparent for microwaves, depending on theprocess. The inner member (3) is connected to the supply of the gas and/or vapour mixture which is pressed through its wall into the space between inner member (3) and inside surface of the container (1). The porosity or perforation of the inner member (3) is designed such that when pressing the gas and/or vapour mixture through its wall it causes a pressure drop large enough for the pressure (p_2) inside the inner body to be too high for plasma ignition and the pressure (p_1) outside of the inner member to be adequately reduced for plasma ignition. For being applicable for containers with a narrow opening, the inner member (3) is preferably made of an elastically extensible material and is designed such that it is inflatable by the pressure difference.



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METHOD AND APPARATUS FOR TREATING INSIDE SURFACES OF CONTAINERS

The invention is in the field of the packaging industry and relates to a method according to the generic part of the first independent claim and to an apparatus for carrying out the method. Method and apparatus serve for treating inside surfaces of containers with a plasma enhanced treatment, in particular for treating containers with narrow openings such as bottles, which containers are made of any material, in particular of a thermosensitive material such as plastic or cardboard.

It belongs to the state of the art to treat surfaces of packaging items or of packaging materials in plasma enhanced processes mainly for depositing barrier layers or other layers with specific functions but also for cleaning, activating and/or sterilizing the surfaces. In many cases the plasma enhanced process is a plasma enhanced chemical vapour deposition or plasma enhanced polymerization but also sputtering and other known processes are applied.

The plasma is ignited in the area of the surface to be treated by establishing in this area an appropriately reduced pressure and an electric field alternating with a high frequency (e.g. 40 MHz) or a field of electromagnetic waves (e.g.

microwaves). For chemical vapour deposition an appropriate mixture of gases and/or vapours is flown through the plasma whereby chemically active particles are formed leading to chemical reactions on the surface to be treated.

Experience shows that the surface quality obtained in such treatment depends considerably on the homogeneity of the electric field or the field of electromagnetic waves and on the homogeneity of the gas and/or vapour concentration in the area of the plasma or of the surface to be treated respectively. Depending on the sort of process and on the arrangement, a large amount of energy is necessary for sustaining the plasma such that the container to be treated is exposed to a considerable heat load, which might restrict the process to containers of little heat sensitivity or might make cooling of the container necessary.

For treating flat substrates, known methods give satisfactory qualities for treated surfaces. As soon as the surface to be treated is not plane, problems are encountered which, according to the application are more or less grave.

In the publications DE-3632748, DE-3908418, WO-95/21948 and WO-93/24243 plasma enhanced processes for the treatment of inside surfaces of containers such as e.g. bottles are described.

DE-3632748 deals with a process for coating plastic containers. These are placed in a vacuum chamber and the open end of a gas/vapour supply tube is placed inside the container and connected to a gas/vapour source whereby the supply tube is insulated against the chamber wall. The chamber is evacuated

and its wall is coupled to a microwave generator. The ignited plasma fills the volume of the whole of the chamber which does not only mean that besides the inside surface of the container also the gas/vapour supply tube, the container outside surface and the chamber wall are treated but it also means high energy consumption; both of which are not desired. This disadvantage is partly prevented if the container to be treated has a sufficient mechanical strength for being evacuated. It becomes then possible not to evacuate the chamber but the container only and therefore the plasma is confined to the inside of the container whereby less energy is consumed and treatment is limited to the container inside and to the gas/vapour supply tube. Furthermore, the chamber does not need to be vacuum tight.

The publication DE-3908418 describes a similar process in which the gas/vapour supply tube is made of a metallic material and serves not only for supplying the necessary gas/vapour mixture to the inside of the container to be treated but also serves as one of two electrodes being coupled to a high frequency generator or as microwave emitter. As already discussed for the process according to DE-3632748, a plasma will be ignited on the inside and on the outside of the container to be treated and in the case of a deposition process deposition will take place not only on the inside of the container but also on its outside surface and on the chamber wall, unless the container is strong enough for being evacuated and/or is metallic and serves itself as electrode or is not transparent for microwaves respectively.

Publication WO-95/21948 describes a similar process for coating the inside surface of containers such as bottles. A vaporizer is placed on the inside of the container and may also serve as gas/vapour inlet tube and as electrode. For obtaining good treatment results, the vaporizer is moved along the container axis and the container is rotated during treatment.

The publication WO-93/24243 describes a process for plasma enhanced treatment of the inside surface of containers in which a plasma is ignited in a separate chamber, an oxidizing gas mixture is flown through the plasma chamber whereby active species are produced and flushed into the inside of the container where they mix with other reactants forming under the influence of an alternating electric field a coating on the inside container surface. For even distribution of the reactive mixture in the container, rotation of the container or movement relative to the inlet of the reactive species and/or of the other reactants is recommended as well as specific arrangements of the inlets for the reactive species and the other reactants. For this method, the plasma volume is not directly correlated to the volume of the container or the chamber respectively and can therefore be reduced to a necessary minimum. On the other hand an electric field must be sustained in the area of the bottle also.

It is now the object of the invention to create a method and an apparatus for treating the inside surfaces of containers, in particular containers with a narrow opening and containers made of a heat sensitive material. Method and apparatus are to make it possible to keep the energy consumption during the plasma enhanced treatment low and therefore the heat load on the container to a minimum. Furthermore, the inventive method is to solve the problem of the even distribution of the reactant gas/vapour mixture in a more simple way than known such methods. The inventive apparatus is to be simple and adaptable for batchwise operation i.e. for simultaneous treatment of a plurality of containers within the same apparatus. Furthermore the inventive apparatus is to be easily adaptable for different shapes and sizes of containers to be treated.

These objects are achieved with the method and the apparatus as defined in the claims.

According to the inventive method, the plasma is sustained inside the container to be treated either by establishing a high frequency electric field between an electrode placed inside the container and another one outside the container or by placing a microwave emitter inside the container. The plasma does not fill the entire inside volume of the container but is confined between the inner container surface and an inner member placed into the container whereby the inner member is shaped such that it fills the inside of the container but for a thin layer along the container wall with a width over the whole area of the inner container surface of 5 to 15 mm, preferably approximately 10mm which width is as constant as possible. The container is placed in a chamber.

The pressures established in the system are the following: pressure inside the inner member: too high for plasma ignition; pressure between inner member and container wall: appropriately reduced for plasma ignition; pressure outside the container: according to mechanical strength of the container, preferably either too high or too low for plasma ignition.

The inner member such serves for confining the plasma within a narrow layer along the inner container surface. Furthermore it serves as supply device for supplying the gas/vapour mixture necessary for the plasma enhanced treatment. It is therefore hollow and perforated or porous, i.e. causing a predetermined pressure drop in a gas stream pressed through its wall perforation or through its pores. For being applicable for treating containers with a narrow opening or mouth, it is furthermore preferably inflatable from a

narrow shape introducible through the container opening to an operative inflated shape adapted to the shape of the inside of the container, whereby the supply pressure of the gas/vapour mixture keeps the inner member in its operative inflated shape. It may also have its operative shape without an inner over pressure and be brought into a narrow shape by an reducing its inner pressure.

The perforation or porosity of the inner member is designed such that sufficient gas/vapour flows from the inside of the inner member to its outside at a pressure difference which is high enough for preventing plasma ignition on the inside of the inner member and allowing plasma ignition on the outside.

The inner member is made of a material totally transparent for microwaves or other electromagnetic waves employed or for an electric field. An electrode or wave emitter (e.g. microwave emitter) is placed on the inside of the inner member.

For establishing a gas/vapour concentration in the plasma being as homogeneous as possible, the perforation or porosity of the wall of the inner member forms a regular pattern over the surface of the inner member. If the plasma area, e.g. due to a complicated shape of the container to be treated, contains regions of different widths, the perforation pattern is designed such that in regions of wider plasma (larger distance between inner member and container wall) accordingly more gas/vapour passes through the wall of the inner member due to more and/or larger perforations or pores in this area.

It is shown that using the inventive method for e.g. depositing an inorganic barrier layer of e.g. SiOx or AlOx on the inside surface of plastic bottles, high quality results are achieved firstly due to the homogeneity of the conditions over the whole inside surface of the container and secondly due to the low energy consumed eliminating the risk of damage to coating and/or container caused by heat or arcing.

The inventive method and the inventive apparatus are to be described in more detail in connection with the following Figures, wherein:

Figure 1 shows the principle of the inventive method and of the inventive apparatus and

Figures 2 and 3 show two exemplified inner members for specific applications in more detail.

Figure 1 shows the principle of the inventive method with the help of a diagrammatic section through an exemplified embodiment of the inventive apparatus. The container 1 to be treated is positioned inside a chamber 2 which chamber is openable (not shown) for introduction of the container 1 and is connected to a vacuum pump (not shown) for controlled evacuation. The mouth of the container 1 is closed towards the chamber and is also connected to a vacuum pump (not shown) for controlled evacuation of the container 1. Inside the container an inner member 3 is shown in its inflated operational state (3) and in its deflated narrow state (3'), which deflated state enables it to be introduced through the mouth of the container. The mouth of the inner member 3 is connected through the mouth of the container to an arrangement 6 for quantitative preparation of the gas/vapour flow from gas and/or vapour supply vessels 6' or similar sources. On the inside of the inner

member 3 there is an electrode or emitter 4 connected through the mouth of the inner member to a high frequency voltage source 5 or to a microwave generator respectively.

Chamber 2 consists e.g of two parts, a support part in which the vacuum connection to the container 1, the inner member 3 and its supply connection and the electrode or emitter 4 respectively are installed permanently and a cover part tightly positionable on the support part. The chamber 2 may be equipped for simultaneous treatment of a plurality of containers, i.e. comprise a plurality of adequately spaced inner members with electrodes or emitters.

The inventive method is carried out as follows: Gas/vapour supply to the inner member 3 is stopped and therefore the inner member is deflated either by loss of overpressure or actively by evaporation. The chamber 2 is opened and a container is positioned over the inner member 3 and its mouth is locked onto the corresponding vacuum connection. The chamber 2 is closed and chamber 2 and container 1 are simultaneously evacuated. Then gas/vapour supply and power are switched on and thereby the inner member 3 is inflated and the plasma ignited by means of the alternating field or the field of electromagnetic waves. Under these conditions and with a controlled flow of gas/vapour mixture from the inner member 3 through the plasma area into the exhaust (vacuum connection) of the container the container is treated for a predetermined time. Then the power is switched off and the system flushed, the chamber 2 is opened and the container 1 is removed.

For adapting the apparatus for treating containers of a different form it is only the inner members and, if necessary, the vacuum connection to the container mouth which need to be exchanged.

Working pressures are e.g.: p_1 in the plasma area between inner member and container wall: between 10^{-3} and 10^2 mbar; p_2 inside the hollow inner member: between 10 and 100 mbar; p_3 in the chamber: lower than 10^{-3} or higher than 100 mbar.

If the container is mechanicly strong enough p_3 can be equal to ambient pressure and the chamber can be open to atmosphere or can even be omitted provided that, when using microwave the container is impermeable for microwaves.

As mentioned before, the inventive method and the inventive apparatus are applicable for various plasma enhanced treatments for coating, cleaning, activating and/or sterilizing the inner surface of the container. One example of such a treatment is coating containers of plastic material such as e.g. polyethylentetraphthalate, PEN, polyethylene, polyamide or polypropylene with a silicon oxide. This coating is carried out as a plasma enhanced chemical vapour deposition using a gas/vapour mixture consisting of an organosilicon compound (e.g. hexamethyldisiloxane, 1,1,3,3-tetramethylsiloxane, methyldimethoxisilane, vinyltrimethylsilane or vinyltrimethoxisilane), oxygen and an inert gas such as helium or argon.

In similar processes other inorganic or organic compounds are deposited on containers not only of plastic materials but also of e.g. cardboard, paper, metal, ceramic or glass. All these processes are applicable for treating inside surfaces of containers according to the inventive method.

If the plasma enhanced process is a coating process coating of the inner member cannot be prevented. If though the inner member is inflated and deflated between successive coating cycles, the coating of the inner member is removed by this deformation as soon as it has achieved a critical thickness. Therefore such an inner member is automatically self-cleaning.

Figure 2 shows in section and in more detail than Figure 1 an exemplified inner member 3 for treating a container 2 with a specific inside shape. The inner member 3 is shown in its inflated operational state and in its deflated state (3', in dash-dotted lines) in which the member is introduced through the mouth 11 of container 1. The inner member 3 is made of an elasticly extensible material, e.g. a polymer material. Its change of shape with increasing pressure difference is determined e.g. by its local thickness, which is higher in areas where it is to stretch little and is lower in areas where it is to stretch more. It is porous or perforated with a fine pattern of perforations, whereby it is advantageous to provide more and/or larger perforations in areas in which the gap between container wall and inner member is larger (areas A).

Preferably the material of the inner member 3 is chosen in such a way that the member is self supporting at least in its deflated state.

Figure 3 shows also in section a further exemplified inner member 3 positioned in a container 1 to be coated on its inside surface. The inner member 3 consists of a porous material, e.g. of a polymer foam. The shape of the inner member is adapted to the inner shape of the container. For introducing the inner member into the container or for removing it from the container, vacuum is applied to the inner member through the supply tube 30

connected to the inner member. By the effect of the vacuum the pore size in the member is reduced and therefore the overall size of it also.

CLAIMS

1. Method for treating the inside surface of a container (1) with an opening in a plasma enhanced process in which a plasma is sustained inside the container and a process specific gas and/or vapour mixture is flown through the plasma, **characterized** in that the plasma is confined between the inner surface of the container (1) and a hollow inner member (3) with a shape adapted to the inside shape of the container (1) by supplying the gas and/or vapour mixture to the inside of the inner member (3), pressing it through the wall of the inner member (3) into the space between the inner surface of the container and the inner member (3), whereby the wall of the inner member (3) is porous or perforated to cause a predetermined pressure drop, and by evacuating the space between the inner member (3) and the inner surface of the container (1) such establishing in this space a reduced pressure (p_1) suitable for plasma ignition and on the inside of the hollow inner member (3) a pressure (p_2) which is too high for plasma ignition.

2. Method according to claim 1, **characterized** in that the space between the inner surface of the container (1) and the inner member (3) is 5 to 15 mm wide.

3. Method according to claim 1 or 2, **characterized** in that the inner member (3) is inflatable and is introduced into the opening (11) of the container (1) in its deflated state and is then inflated to take its operational shape by the gas and/or vapour supply.

4. Method according to claim 1 or 2, **characterized** in that the inner member (3) is deflatable by applying vacuum to its inside.

5. Method according to one of claims 1 to 4, **characterized** in that the container (1) to be treated is placed in a chamber (2) and that the chamber is evacuated simultaneously with the evacuation of the container (1).

6. Method according to one of claims 1 to 5, **characterized** in that the plasma is ignited with the help of a microwave emitter (4) positioned on the inside of the inner member (3).

7. Method according to one of claims 1 to 5, **characterized** in that the plasma is ignited with the help of an electrode (4) on the inside of the inner member (3) and an electrode on the outside of the container (1) and that one of the electrodes is connected to an alternating voltage and the other electrode is connected to earth.

8. Method according to one of claims 1 to 7, **characterized** in that the container (1) is made of plastic or of cardboard and that the plasma enhanced process is a plasma enhanced chemical vapour deposition of siliconoxide or of aluminiumoxide.

9. Apparatus for carrying out the method according to one of claims 1 to 8 which apparatus comprises means (4/5) for establishing an alternating

electric field or a field of electromagnetic waves at least within the container (1) to be treated, means (6/6') for controlled supply of a gas and/or vapour mixture to the inside of the container (1) to be treated and means for evacuating the container, **characterized** in that the means for the controlled supply of a gas and/or vapour mixture to the inside of the container (1) comprises an inner member (3), which inner member (3) is hollow and adapted in shape to the inside shape of the container (1) and has a perforated or porous wall to cause a predetermined pressure drop and which member (3) is introduceable into the opening of the container (1).

10. Apparatus according to claim 9, **characterized** in that between the inner member (3) and the inner surface of the container (1) there is a space which is between 5 and 15 mm wide.

11. Apparatus according to claim 9 or 10, **characterized** in that the wall of the inner member (3) consists of an elasticly extensible material such that the inner member (3) is inflatable by the supply pressure of the gas and/or vapour mixture.

12. Apparatus according to claim 9 or 10, **characterized** in that the inner member is deflatable by application of vacuum.

13. Apparatus according to one of claims 9 to 11, **characterized** in that it further comprises a chamber (2) in which the container (1) is positionable and in which the pressure is reduceable.

14. Apparatus according to one of claims 9 to 12, **characterized** in that the means for establishing an alternating electric field or a field of electromagnetic waves respectively inside the container (1) comprises an electrode or emitter (4) respectively positioned inside the inner member (3).

15. Apparatus according to claim 14, **characterized**, in that the emitter (4) is a microwave emitter.

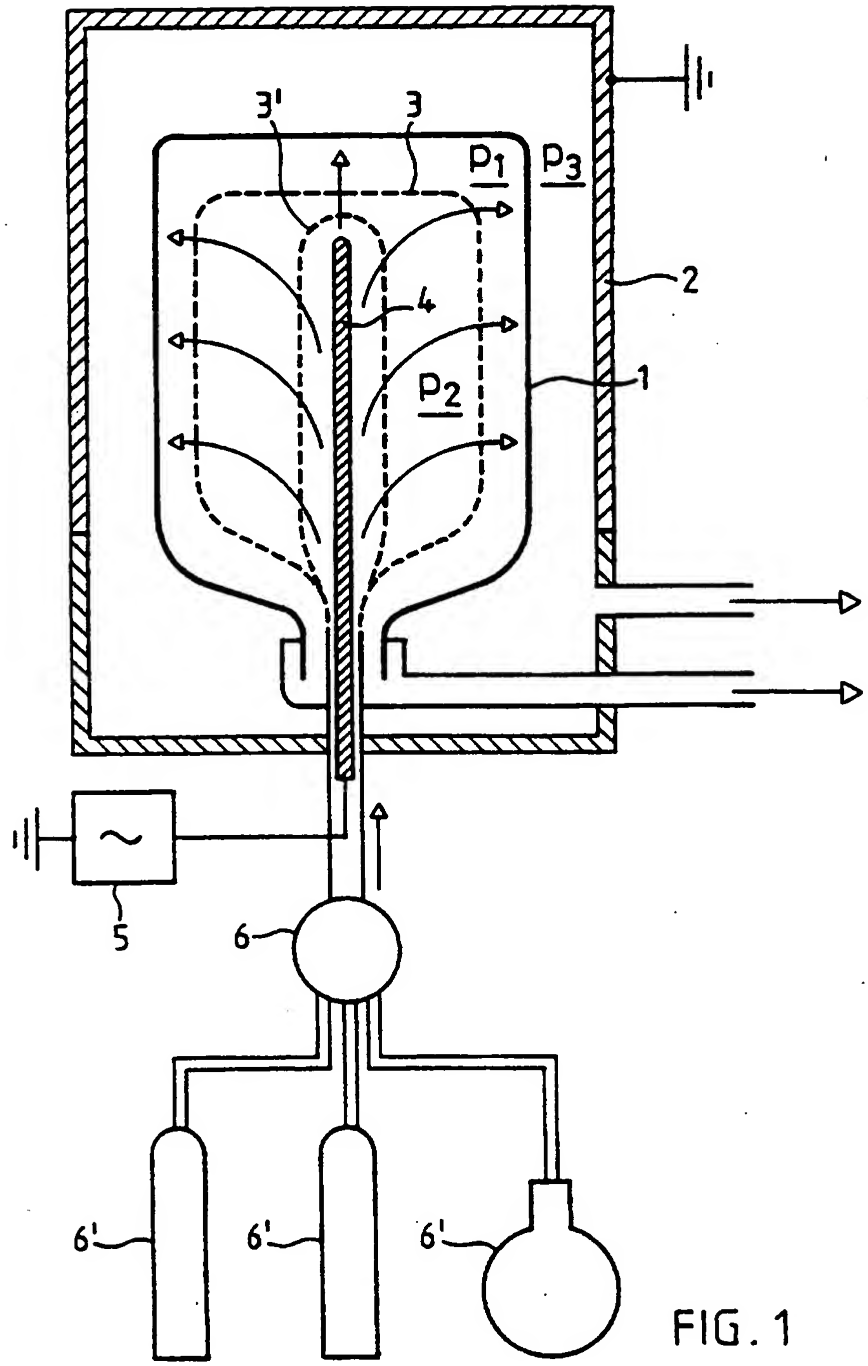

FIG. 1

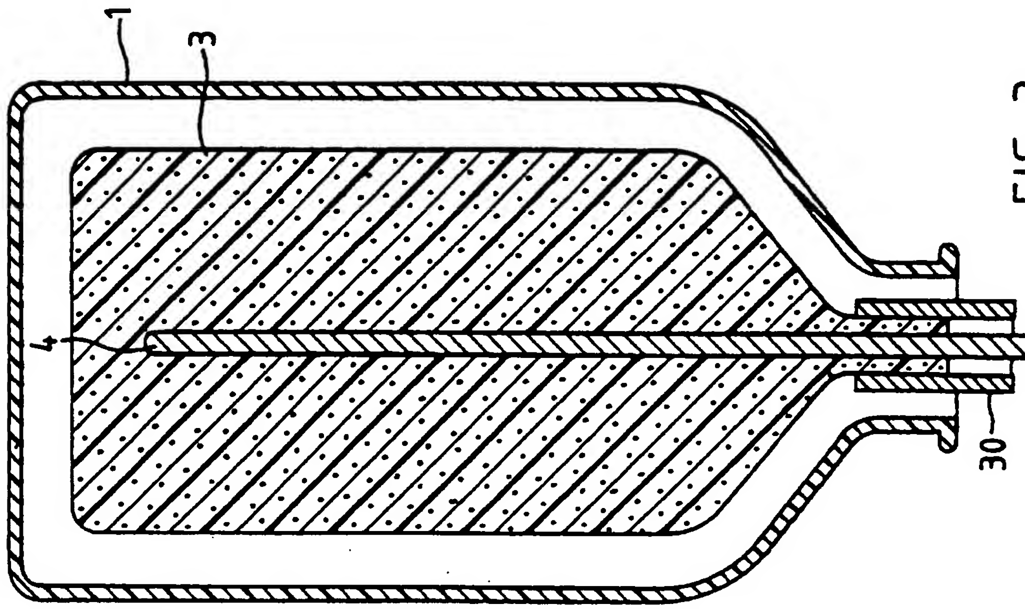

FIG. 3

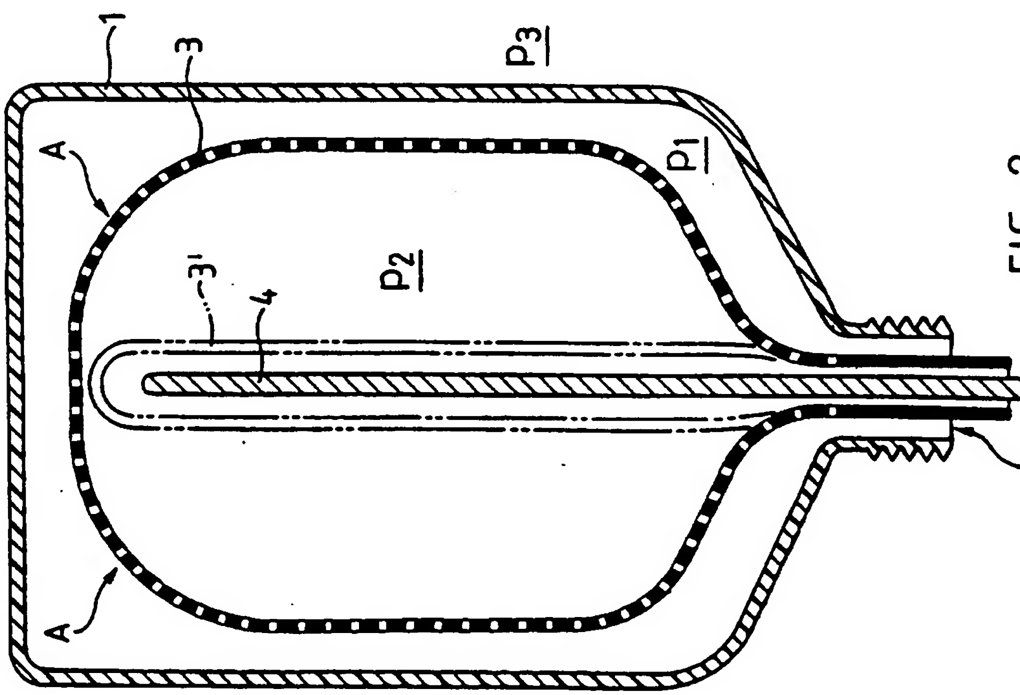

FIG. 2

INTERNATIONAL SEARCH REPORT

Internat Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C16/04 C23C16/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 40 08 405 C (SCHOTT GLASWERKE) 11 July 1991 see claims 1,7; figures 1-5 ---	1,9
A	WO 94 00247 A (POLAR MATERIALS INC) 6 January 1994 see figures 1,2 ---	1,9
A	DE 43 18 084 A (KAUTEX WERKE GMBH ;PLASMA ELECTRONIC GMBH (DE)) 8 December 1994 see column 5, line 49 - column 6, line 62; figure 3 -----	1,9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4008405 C	11-07-91	CA 2038292 C	18-04-95
		CN 1055015 A	02-10-91
		DE 59103456 D	15-12-94
		EP 0446596 A	18-09-91
		JP 4224681 A	13-08-92
		US 5154943 A	13-10-92
		US 5236511 A	17-08-93
WO 9400247 A	06-01-94	US 5308649 A	03-05-94
		AU 658329 B	06-04-95
		AU 4640493 A	24-01-94
		BR 9305550 A	22-11-94
		CA 2112103 A	06-01-94
		EP 0605703 A	13-07-94
		JP 6510234 T	17-11-94
		PL 302288 A	11-07-94
		US 5374314 A	20-12-94
DE 4318084 A	08-12-94	CA 2164223 A	08-12-94
		WO 9427745 A	08-12-94
		EP 0705149 A	10-04-96
		EP 0778089 A	11-06-97